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SINGLE CRYSTAL GALLIUM PHOSPHIDE SOLAR CELLS*

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Introduction

Photovoltaic energy converters are of interest for space utilization. Silicon has been the most widely used material for these applications. In recent years consideration of optimum energy-gap materials has led to the study of gallium arsenide for photovoltaic utilization. Since higher temperature operation of solar cells is desired there has also been increasing interest in higher energy gap III-V compounds such as GaP. This report is concerned with some optical, electrical and thermal characteristics of experimental solar cells fabricated from epitaxially grown single crystal GaP.

Experimental Procedures

Material Preparation and Properties

Single crystal gallium phosphide was synthesized from the elements by vapor transport and epitaxial deposition on single crystal gallium arsenide substrates. The transport gas* was a dilute mixture of hydrogen chloride in hydrogen. The reaction was carried out in a 20 mm I. D. quartz tube in a furnace system having three individually controlled zones. Phosphorus* was evaporated into the gas stream at temperatures from 400° to 450°; gallium* was held at temperatures from 890° to 975° with the substrates between 790° and 870°. Temperature gradients in the deposition zone ranged from 3°C/cm to 25°C/cm. Typically, the total gas flow was 300 cc/min with a hydrogen to hydrogen chloride volume ratio of 150, although in some experiments hydrogen flow rates were varied from 155 cc/min to 800 cc/min and hydrogen chloride flow rates in the <100> direction ranged from 0.1 to 0.2 microns/cc HCl but fell as low as 0.03 microns/cc HCl at lower H_2/HCl ratios and at the lowest phosphorus pressures. The growth rate depends on both temperature and on temperature gradient in the deposition zone.

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* Prepurified hydrogen and anhydrous hydrogen chloride were obtained from the Matheson Company. Red Phosphorus of semiconductor grade from the American Agricultural Chemical Company or from L. Light and Col, Ltd. Gallium of 99.9999% purity was obtained from Alcoa.

Thicknesses of the single crystal epitaxial GaP varied from about 10 microns to about 200 microns with the majority of the GaP material having thicknesses of the order of 40 microns.

The surfaces of the gallium phosphide layers were generally poor, containing many bumps and other defects, however, no effect on solar cell properties has yet been detected. The best surfaces were prepared at lower growth rates. Surface appearance depends on substrate surface preparation, orientation and run conditions. A significant improvement was achieved by pretreating the substrate at $1000^{\circ}C$ in phosphorus vapor carried by hydrogen just prior to deposition of gallium phosphide.

Electrical properties of the layers were obtained by measurement of Hall constant and resistivity of Hall bars located adjacent to the wafers during deposition. Typical values for mobility and net carrier level of "undoped" <100> grown material were 100 cm^2 $volt^{-1}$ sec^{-1} and $2 \times 10^{16} cm^{-3}$ respectively. A total ionized impurity level in the 10^{18} range is indicated in all samples.

Sample Preparation and Cell Fabrication

The sample areas were typically of the order of 0.2 to 0.5 cm^2 and rectangular with the epitaxial GaP layers having n-type conductivity. Shallow p-n junctions of the order of 1μ or less were formed by zinc diffusion (with phosphorus added) in closed tubes at approximately $800^{\circ}C$ for short times. Following the diffusion, the junction depth was determined by cleaving and etching delineation techniques and the surface concentration deduced from Hall effect measurements. The back surface was lapped back. A contact of Au-Sn-Ni was used on the back surface and silver was evaporated on to the p surface while the sample was held at $200^{\circ}C$ for the p surface contact. The cells were lapped, cleaned and etched to remove any shorting paths around the edges.

Electrical Measurements

The conversion efficiency open circuit voltage and short circuit current measurements were made in bright sunlight using secondary standard silicon solar cells for light intensity calibration. Preliminary electrical measurements however were usually made with a nominal $2800^{\circ}K$ tungsten light source filtered through three inches of water. The voltage was measured with an Applied Physics electrometer. Currents were measured with a Hewlett Packard Microvoltammeter Model No. 425A. The cell area was determined from its length and width which were measured with a traveling microscope.

Optical Measurements

The spectral response measurements were made on a Bausch and Lomb

monochromator Cat. No. 33-86-40 with a plane circular grating blazed for 0.5µ.

The experimental procedure followed was a standard method. The source used was a tungsten lamp. The solar cell was mounted so that it was in the exit beam of the monochromator. A constant slit of 2 mm was held during the entire scan for the solar cell and a Reeder thermocouple in the wavelength interval of 0.35 to 0.9µ. The scan was made first with the solar cell and then with the thermocouple as a detector with all other conditions held constant. A ratio was then taken between the response of the solar cell and the thermocouple and plotted as relative response.

Thermal Measurements

The solar cell, for temperature measurement of the electrical parameters, was mounted in a cell holder of lavite with provisions for Chromel-Alumel thermocouples under and near the solar cell. The cell holder was inserted into a cylindrical muffle furnace. The source used was either a tungsten source or sunlight. In the case of the tungsten source, it was mounted directly on the furnace and focused through an opening in the cell holder on the solar cell. The tungsten source used was a G. E. projector spotlight 150 PAR/SP.

Results and Discussion

Two main types of solar cells have resulted in this investigation: (1) an extrinsic cell having its main spectral response at room temperature in a broad band roughly centered at about 0.75 microns, (2) an intrinsic cell having its principal response at about 0.45 microns. The typical spectral response curves for these cells are shown in Figure 1.

The differences in electrical, optical and thermal characteristics of the two classes of cells are shown in Table I for cells NA31 and NA22 SC21-3 which are examples of the intrinsic and extrinsic cells respectively.

The extrinsic cell is characterized by about half the op circuit voltage and about three times the short circuit current density thus far found for the intrinsic cell. The short circuit current density of the intrinsic cell increases with temperature, doubling at about 275°C, whereas the extrinsic cell shows little change in short circuit current until about 200°C where it decreases rapidly. The open circuit voltages of both cells show the characteristic decrease with increasing temperature and the temperature coefficients are not appreciably different, being of the order of 3 mv/deg. However, at 150°C the voltage of the extrinsic cell has decreased to less than .4 volt. At higher temperatures the intrinsic cell is far superior to the extrinsic cell.

A conversion efficiency of about 1% in bright sunlight at room temperature has been obtained for the intrinsic cell. Somewhat higher values, 1.6%, have been noted for the extrinsic cell.

An E-I power curve taken in sunlight for a solar cell of the intrinsic type, NA31, SC34-3, at t = 23°C is shown in Figure 2 with an input of 04 mw/cm² as deduced using a standard silicon solar cell. An efficiency of about 1% has been obtained.

Open Circuit Voltage vs. Temperature

A parameter of interest is the temperature coefficient of the open circuit voltage, β. The temperature coefficient of the intrinsic cells is found to be about 3 mv/deg for most of the samples. This agrees with that calculated from solar cell theory, assuming an ideal junction and with the energy gap assumed to provide the main variation with temperature. In Figure 3 we have indicated the calculated V_{oc} vs. temperature curve and the experimental results obtained for GaP. It is noted that the absolute value of V_{oc} for the best cell is about 0.3 volts below that calculated from simple theory and this difference holds true throughout the temperature range shown in Figure 3. The difference cannot be easily accounted for in terms of lifetime of diffusion length as permitted by simple theory. Additional effects such as recombination type currents, etc., as pointed out by Wysocki and Rappaport[1] are in the right direction as expected.

At lower temperatures (<150°C) there appears to be some deviation from a straight line in the experimental open circuit voltage-temperature curves. This bending is generally noted around room temperature. It could be related to surface effects, although this has not been established.

With improved material and fabrication processing it is hoped that better agreement in V_{oc} between experiment and theory can be achieved as noted for silicon and GaAs. The three materials and the theoretical and experimental data for the open circuit voltage with temperature are shown in Figure 4[2]. It is of interest to note the difference in magnitude of open circuit voltage between the extrinsic and intrinsic cells as a function of temperature. The slopes of these curves are however similar and about 3 mv/deg. A comparison of the two types of cells is shown in Figure 5.

Short Circuit Current Density vs. Temperature

The short circuit current density of the intrinsic GaP solar cell increases with temperature following a relationship which can be expressed as

$$J_{sc} \sim e^{\frac{-\Delta E}{kT}}$$

B-4.4

where ΔE the activation energy is of the order of 0.05 ev.

In the case of the extrinsic cell the short circuit current density is independent of temperature of $200°C$, decreasing after that.

Typical curves for both types of cells are shown in Figure 6.

Effect of GaAs Substrate

With the thin (40 micron) epitaxial layers and the relatively large areas desired, the GaAs substrate has been retained as a support. The possible effect of the GaP-GaAs interface on the GaP solar cell has been examined.

The procedure involved was to etch out a portion of the GaAs from zinc diffused GaP cells to provide a window directly to the back of the GaP n layer. The GaAs was masked with black wax except for the portion to be etched away. The etch used was 1 HF : 3 HNO_3 : 2 H_2O. This etch attacks GaP only negligibly.

A sketch of the sample with contacts is shown in Figure 7. Contact 2 is the original back contact of Au-Sn-Ni, contact 3 to the GaP, is made in the same manner. Contact 3 is, as can be seen, smaller than the "window". The top contact 1 employs evaporated silver.

If a photovoltage is developed at the GaP-GaAs interface, open circuit voltages and short circuit currents measured between contacts 1 and 2, which include this interface, should differ from those measured between contacts 1 and 3, which do not. No differences have been noted on making the measurements under a variety of conditions including normal solar cell testing conditions both with our standard test apparatus and in sunlight and with a microscope light using both front and back illumination. These results seemed to indicate that with our method for making material the GaP-GaAs interface does not play a significant role in determining the characteristics of the GaP solar cell.

Diffusion Length Measurements

Using the method of Logan and Chynoweth[3], room temperature measurements of diffusion length have been made on mesas of some of the solar cells. From a plot of $1/C/A$ (capacity/area)$^{-1}$ vs. J_p (photo current density of the cell with reverse bias) the minority carrier diffusion length can be determined. Such a plot is shown in Figure 8, for sample NA16 SC13-6 (from the plot, $L_D = 150$ Å). The values obtained by this method for some of our samples range from about 150 Å to about 5000 Å. Using a carrier diffusion constant of 2.5 cm^2/sec., the values of the diffusion length correspond to values of minority carrier lifetime varying roughly from 10^{-12} to 10^{-10} sec.

Capacity-Voltage Measurements

The junctions prepared from the epitaxial GaP material with our procedure generally seem to follow a $1/C^3$ law dependence. We have been able to fit our capacity-voltage data with expressions of the following type:

$$V_a + V_i = \frac{-qa}{12\epsilon} \quad (\frac{\epsilon}{C/A} - W_I)^3$$

or

$$V_a + V_i = \frac{-qa}{12\epsilon} \quad (\frac{\epsilon}{C/A} - W_I)^2 (\frac{\epsilon}{C/A} + \frac{W_I}{2})$$

where V_a is the applied reverse voltage, V_i is the built in voltage of GaP, q, the electronic charge, ϵ, the dielectric constant, C the capacity of the junction, a, is a concentration gradient, A the cross sectional area of the junction. W_I has been introduced into the equations following Logan and Chynoweth[3], to fit our data. It signifies as expected that the space charge layer of the junction is extremely wide and that in actuality our p-n junction can be better represented by a p-I-n structure. The I layer or W_I is found to vary for our cells from about 150 Å to about 10,000 Å.

I-V Characteristics

From D. C. current-voltage characteristics at 23°C, the factor n in the expression $I = I_o \exp \frac{eV}{nkT}$ for a p-n junction is found to be > 2 (n = 4) for cells which have their main spectral response at 0.45μ whereas for 0.7μ cells, n = 2. The latter suggests from the work of Sah, Noyce, and Shockley[4] that recombination center mechanisms may predominate in the extrinsic cells.

Current-voltage characteristics taken on a Tektronix Oscilloscope No. 536 are shown in Figure 9. These are the best traces obtained for a 0.45μ solar cell and a 0.7μ cell.

0.7μ Extrinsic Solar Cell

While it is believed that the mechanism leading to current generation in the 0.7μ cells must likely involve a two step excitation consisting either of two optical steps or one optical and one thermal step, the nature of the centers responsible for the 0.7μ response in the epitaxial GaP is unknown. The 0.7μ response has been found to occur as a major response, however, when a low hydrogen flow rate is used in the growing of epitaxial GaP.

Since the background level of ionized impurities in our material is 10^{18} cm^3 with net carrier levels of 10^{16}, self compensation is suggested. To achieve the close compensation noted in many of the samples which still remain n-type, it is suggested that a deep donor which could correspond to the 0.7μ level could be present. If this is so, it could be the same as the 0.4 ev donor postulated by Gershenzon and Mikulyak[5] and thought to be due to oxygen. This model remains to be verified.

Acknowledgment

References

(1) J. J. Wysocki and P. Rappaport, J. Appl. Phys., 31, 571 (1960).

(2) The experimental data for Si and the calculated curves for Si and GaAs were taken from Ref. 1; the experimental data for GaAs was taken from A. R. Gobat, M. F. Lamorte, G. W. McIver, IRE Trans. Mil. Electronics, p. 20, Jan., 1962.

(3) R. A. Logan and A. G. Chynoweth, J. Appl. Phys. 33, 1649 (1962).

(4) C. T. Sah, R. N. Noyce and W. Shockley, Proc. IRE, 45, 1228 (1958).

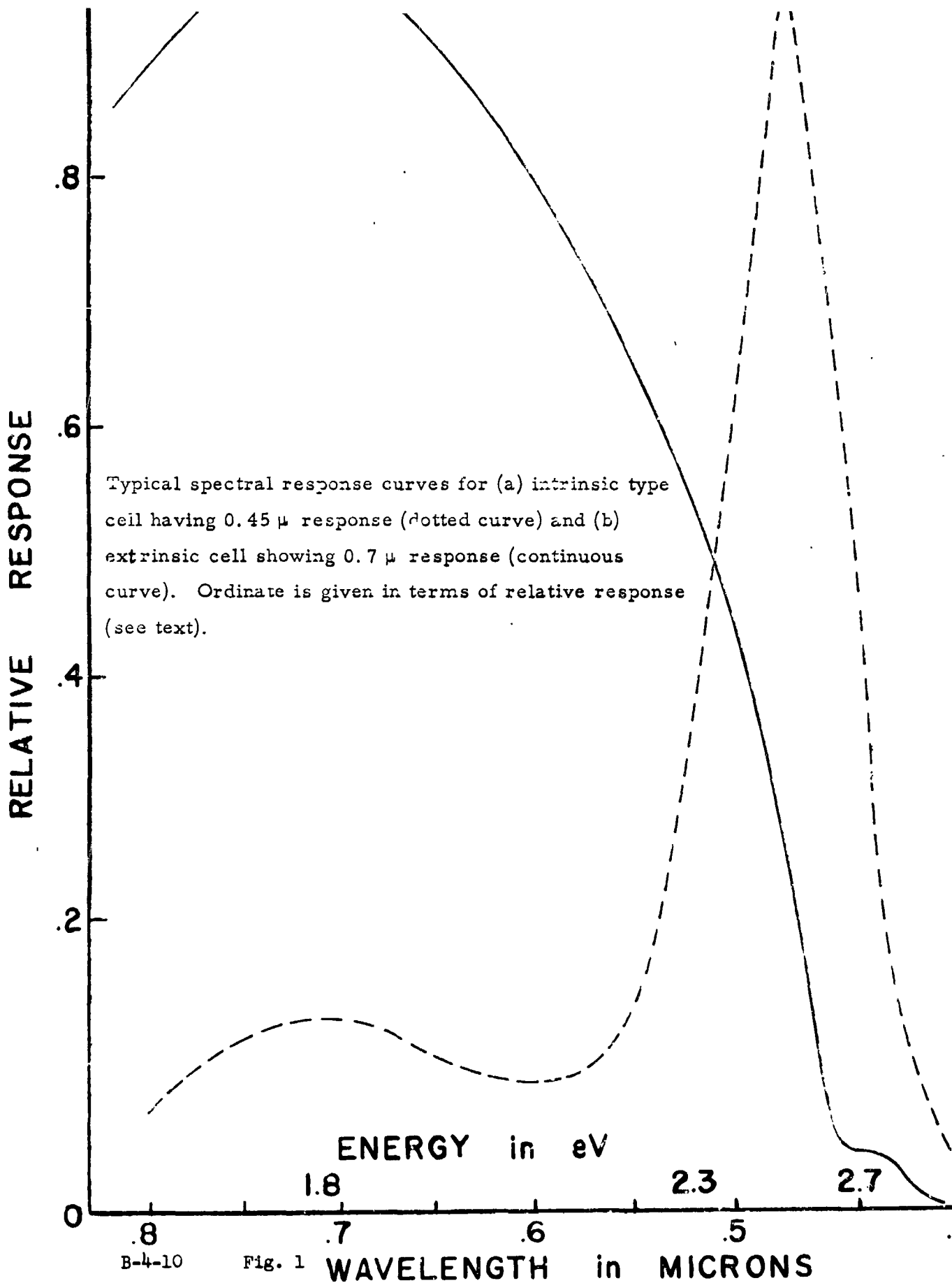(5) M. Gershenzon and R. M. Mikulyak, Solid State Electronics, 5, 313 (1962).

Table I

Characteristics of Extrinsic and Intrinsic GaP Solar Cells

Type:	Intrinsic	Extrinsic
Sample:	NA31 SC34-3	NA22 SC21-3

Electrical:

	Intrinsic	Extrinsic
V_{oc} (volts)	1.35	0.58
J_{sc} (ma/cm^2)	1.4	4.0
Efficiency (measured in sunlight)	1.1*	1.6±

Optical:

	Intrinsic	Extrinsic
Spectral Response Peak (μ)	0.45	0.75 (broad)

Temperature:

	Intrinsic	Extrinsic
Slope J_{sc} vs. 1/T (ev)	.06	0 (to 200°C) J_{sc} decreases after 200°C
V_{oc} vs. T, β (mv/deg)	3.5	2.8
V_{oc} at 300°C	0.23	~ 0
D. C. $I_f - V_f$, $I_o \exp^{eV/nkT}$:	n = 4	2

*   Based on solar intensity as measured with silicon solar cell of 94 mw/cm^2.

±   Based on solar intensity as measured with silicon solar cell of 74 mw/cm^2.

Typical spectral response curves for (a) intrinsic type cell having 0.45 μ response (dotted curve) and (b) extrinsic cell showing 0.7 μ response (continuous curve). Ordinate is given in terms of relative response (see text).
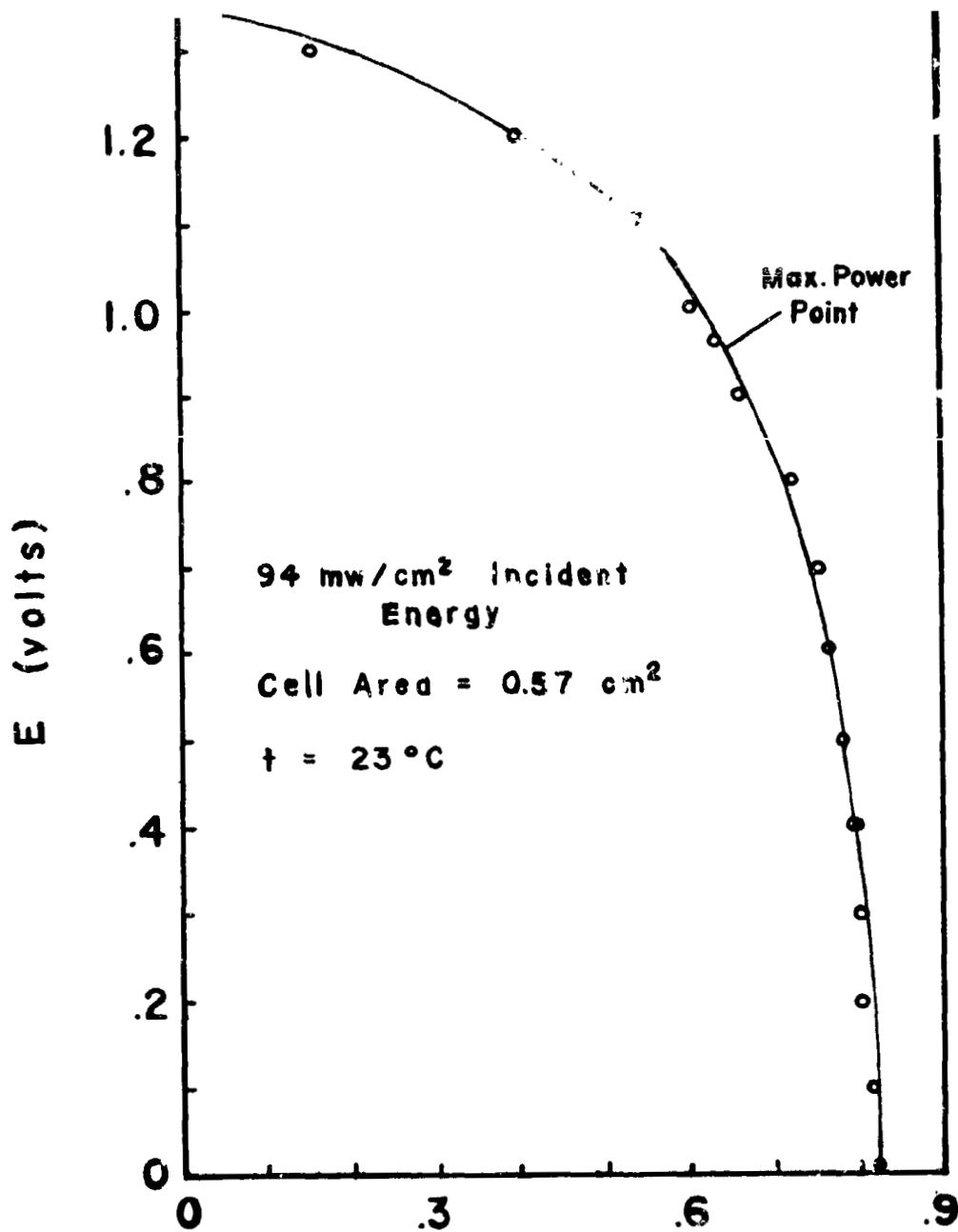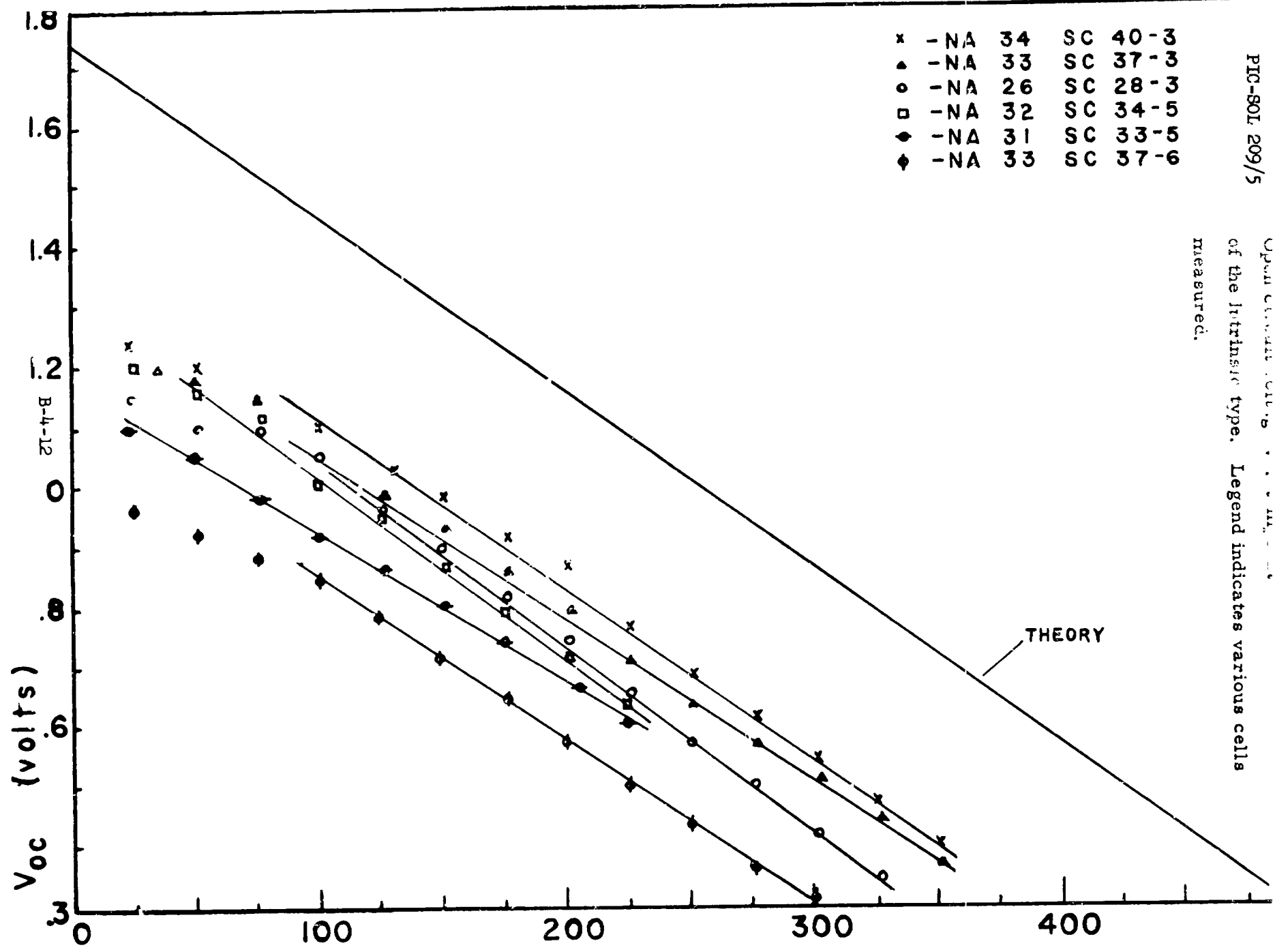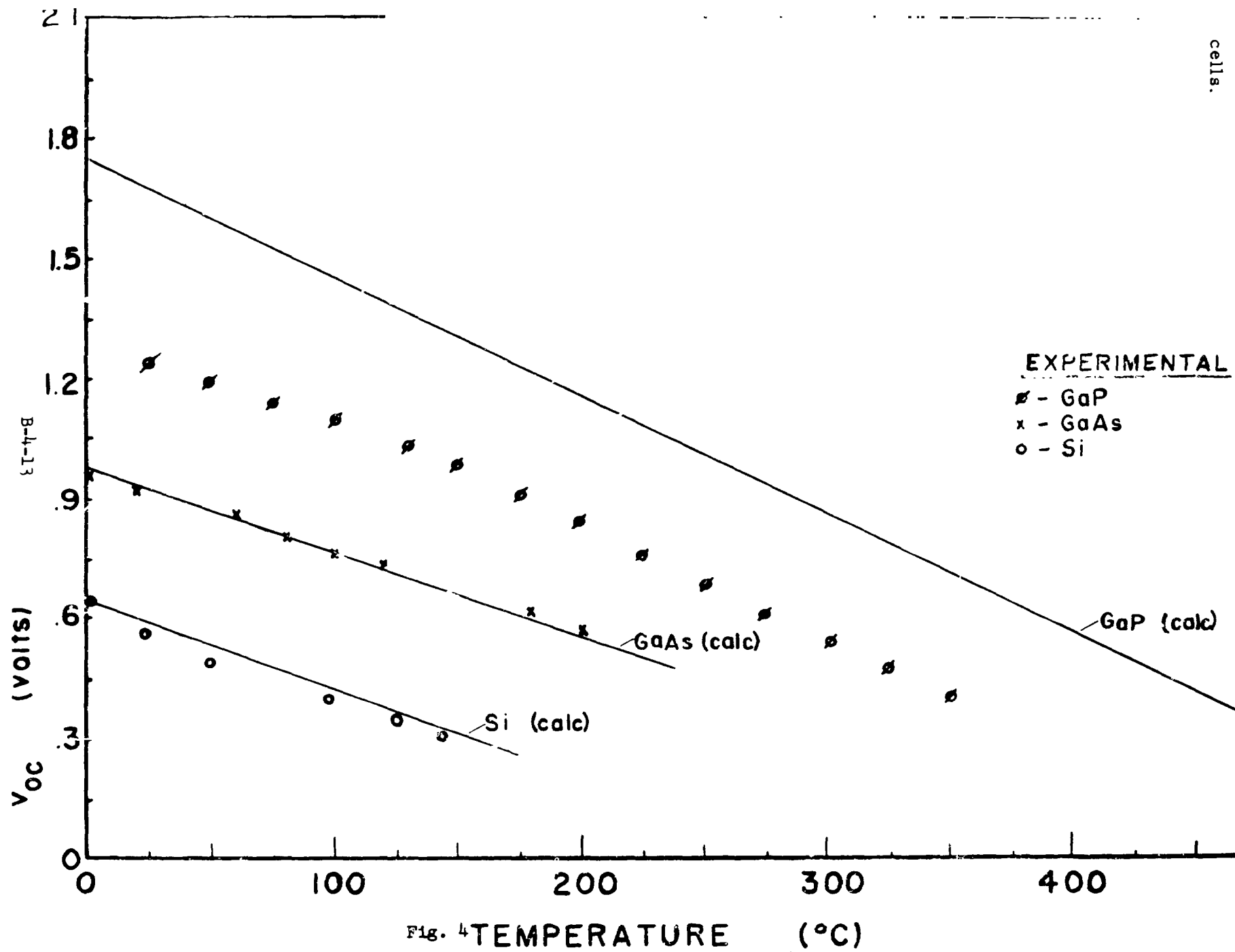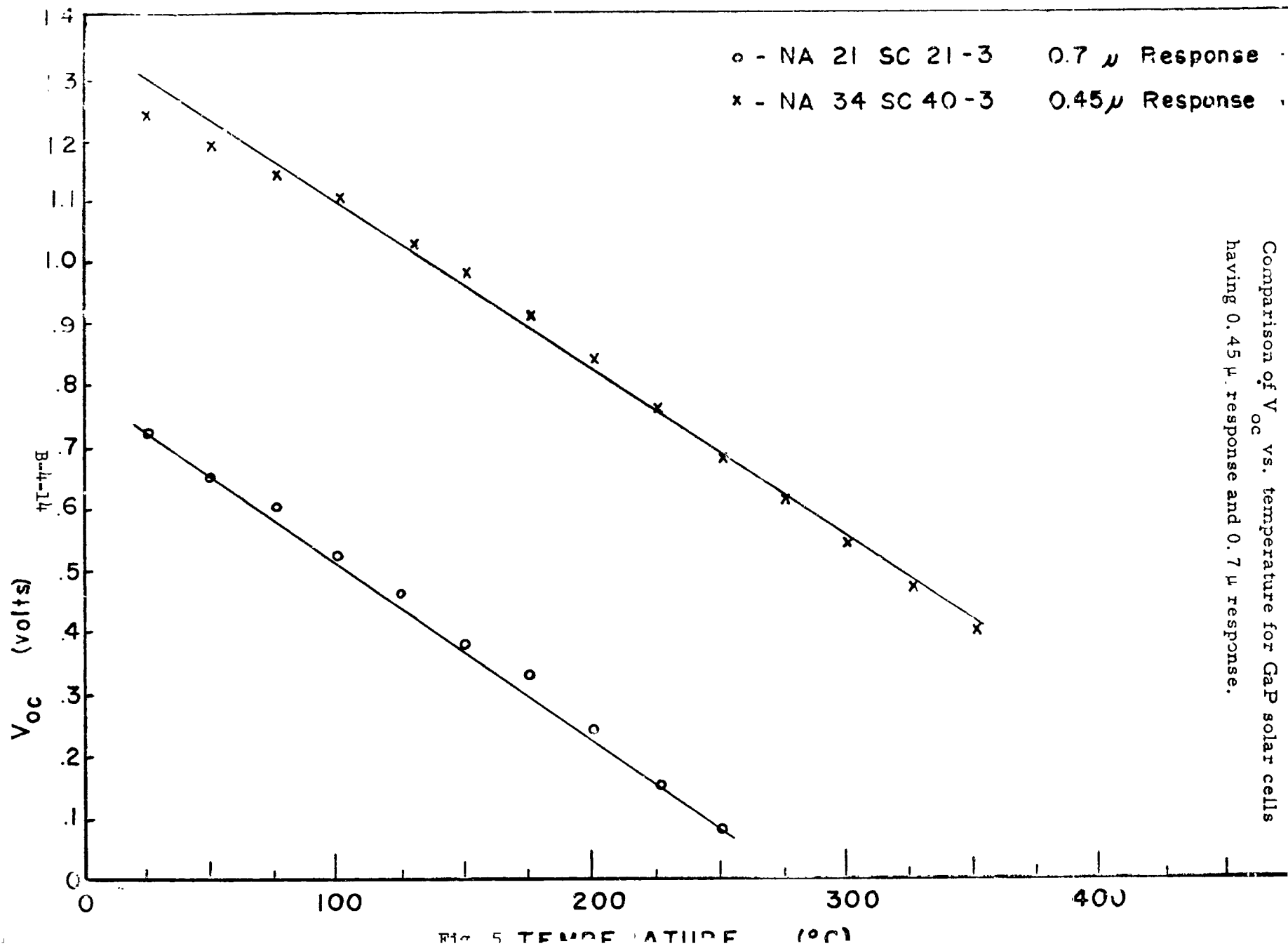
B-4-10   Fig. 1

Fig. 2   I (ma)

Representative E-I curve taken in sunlight for sample
NA31 SC34-3. Sample exhibits main spectral response
at 0.45 μ. Maximum power point is at 0.608 mw.
Efficiency is about 1%. Temperature of measurement
was 23° C.

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Open circuit volts vs thickness of the Intrinsic type. Legend indicates various cells measured.

Legend:
x — NA 34   SC 40-3
▲ — NA 33   SC 37-3
○ — NA 26   SC 28-3
□ — NA 32   SC 34-5
◆ — NA 31   SC 33-5
◆ — NA 33   SC 37-6

THEORY

V_{oc} (volts)

B-4-12

Fig. 4 TEMPERATURE (°C)

EXPERIMENTAL
⌀ – GaP
x – GaAs
o – Si

GaP (calc)

GaAs (calc)

Si (calc)

V_OC (volts)

B-4-13

Comparison of V_{oc} vs. temperature for GaP solar cells having 0.45 μ response and 0.7 μ response.

B-4-14

Fig. 5 TEMPERATURE (°C)

5 —

1

Typical curves of short circuit current density vs.
temperature for both 0.45 μ and 0.7 μ response cells.

2

J_{SC} (ma/cm²)

1 —

.5 —

3

.1 —

.5   1.0   1.5   2.0   2.5   3.0   3.5
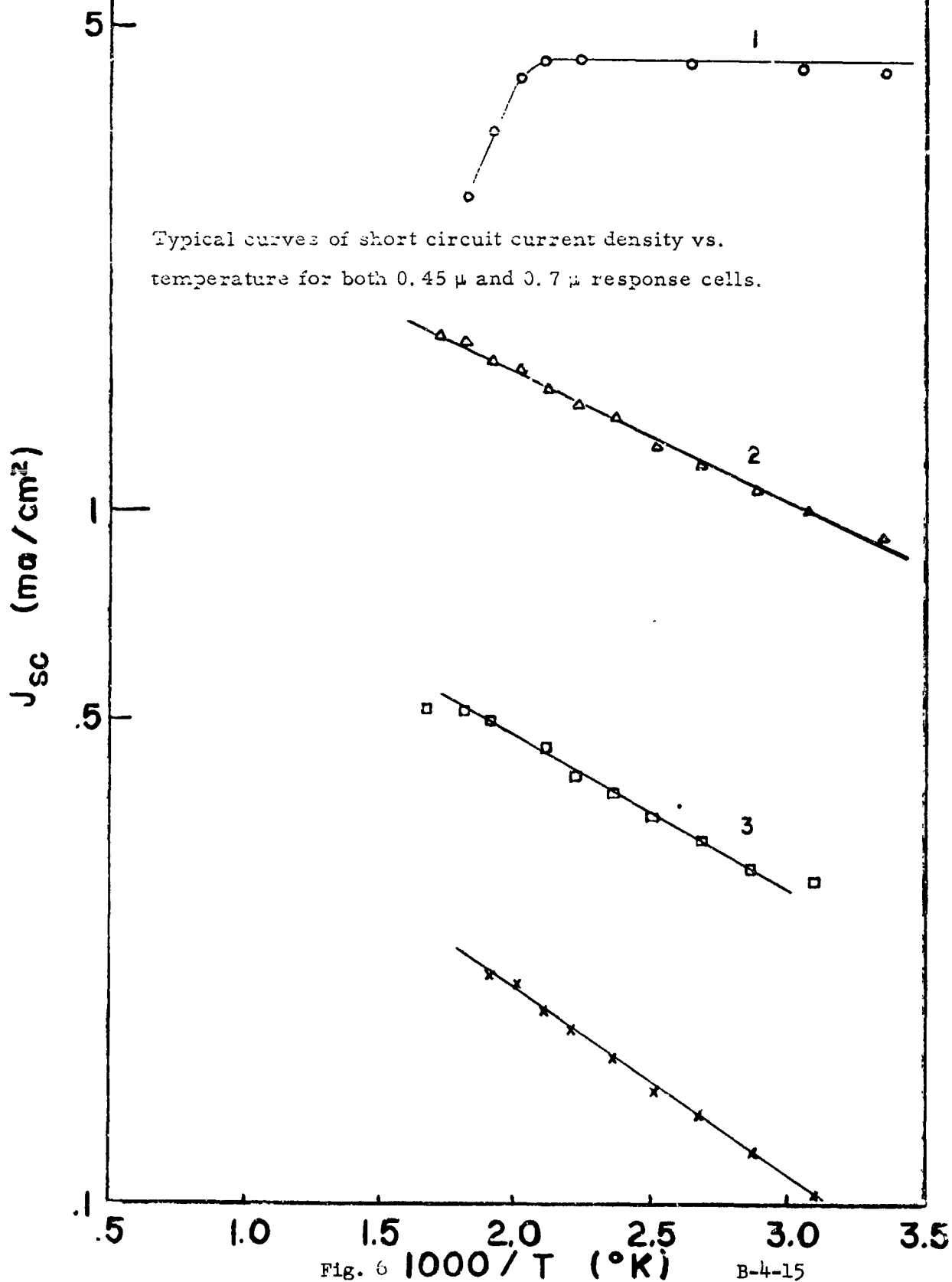
Fig. 6   1000 / T   (°K)   B-4-15
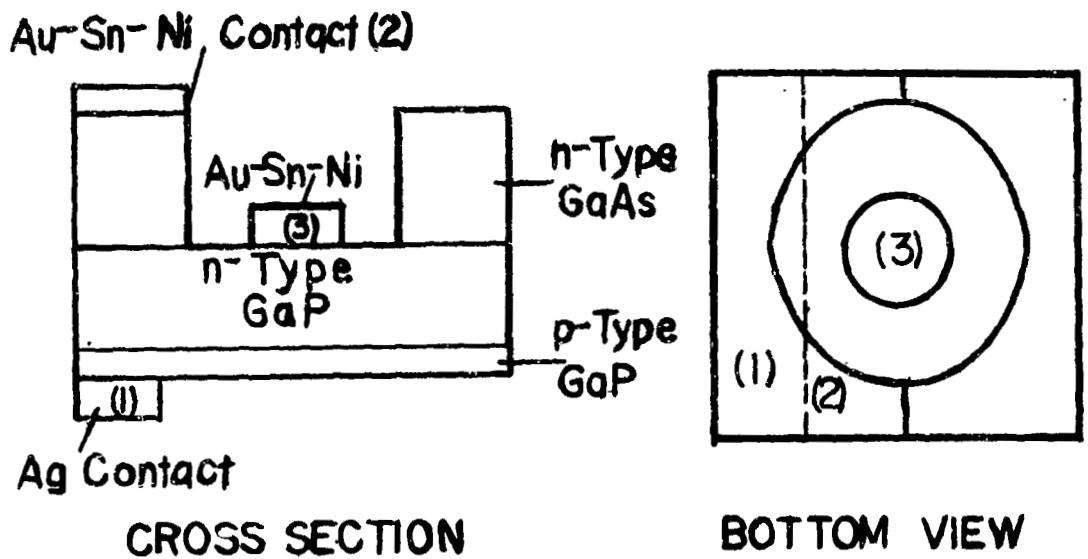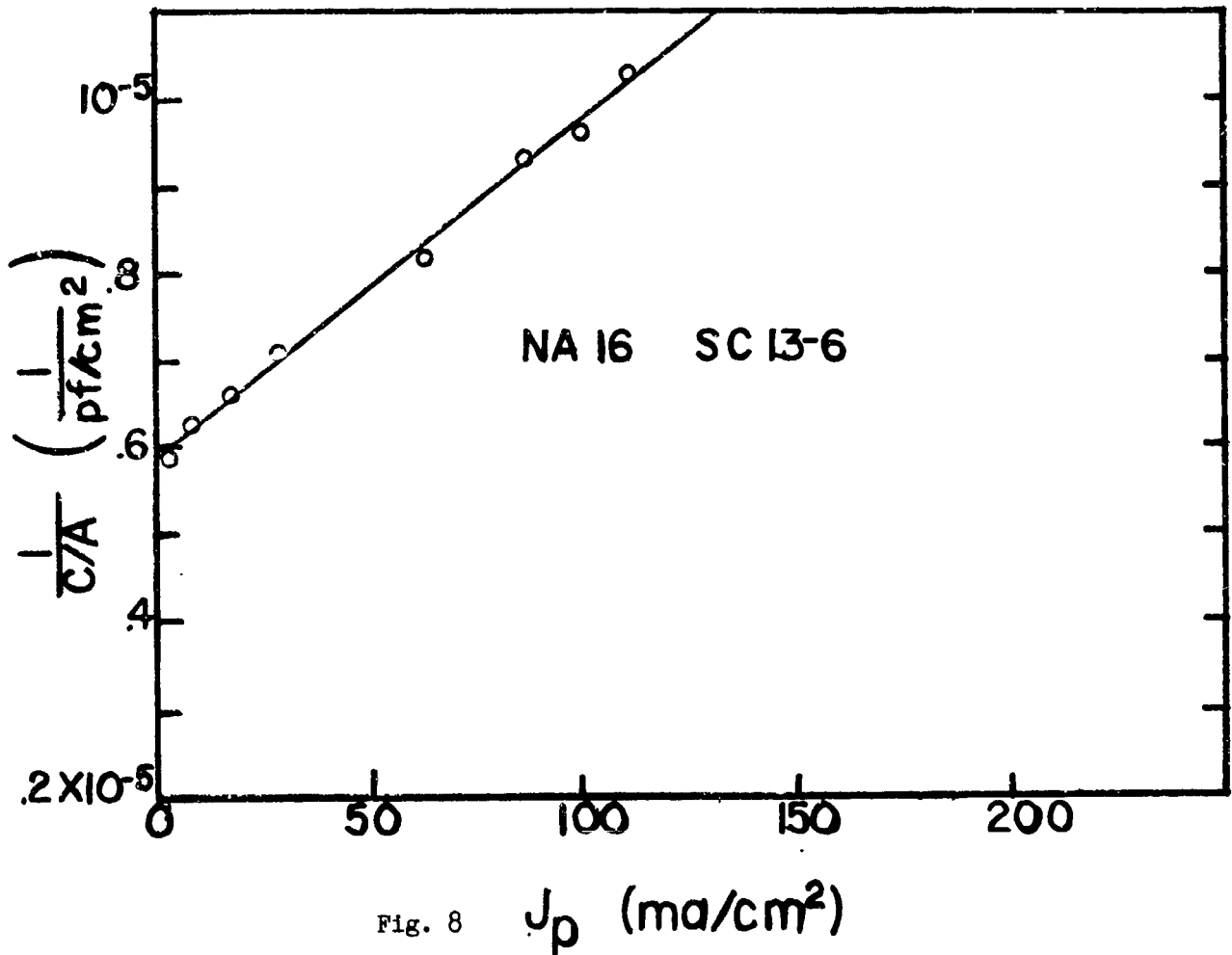
Fig. 7

Experimental arrangement for checking effect of GaP-GaAs interface.
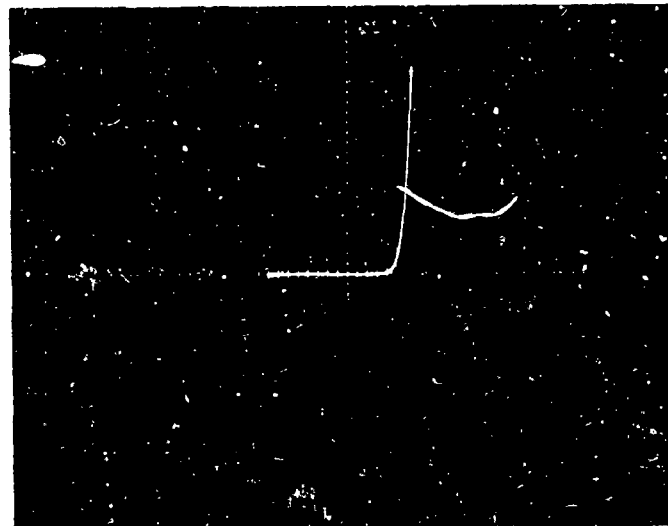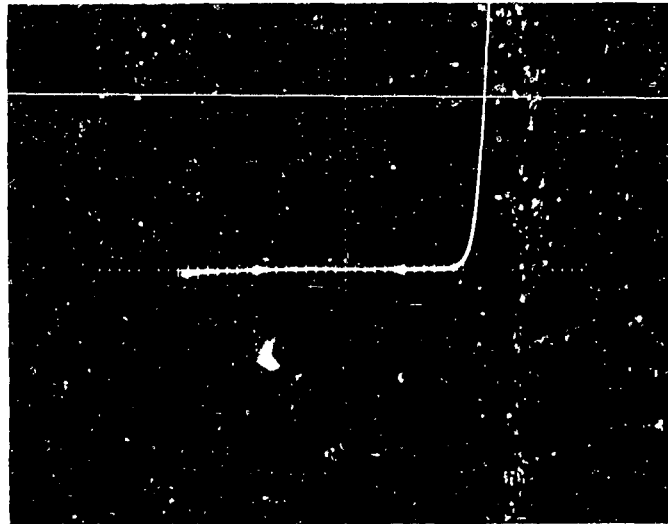
Fig. 8

Sample of plot used for determining minority carrier diffusion length (from plot, $L_D = 150$ Å).

Best current-voltage traces obtained for a 0. 45 μ cell and
a 0. 7 μ cell. Current, vertical axis, 0. 2 ma/cm; Voltage,
horizontal axis, 0. 5 volts/cm for both traces. Top trace,
sample NA32 SC34-5, represents a 0. 45 μ cell. Lower trace,
sample NA22 SC21-3, represents a 0. 7 μ cell.

Fig. 9

B-4-18

DISCUSSION

CHAMBERLIN-NATIONAL CASH REGISTER: Was the cell for which you etched away the GaAs layer, a .7 or .45 micron type?

MR. EPSTEIN: It was a .45 type.

CHAMBERLIN-NATIONAL CASH REGISTER: Did you measure spectral response with both front and back illumination?

MR. EPSTEIN: Yes, we did. They were both the same.

CUSANO-GENERAL ELECTRIC: Grimmeisen did some work on gallium phosphide, and he got efficiencies comparable to yours. He felt that there were series resistance effects, and that an efficiency of 7% could eventually be realized if you could eliminate the series resistance. Do you feel that this is a realistic estimate?

MR. EPSTEIN: Yes, I think it's reasonable.

CUSANO-GENERAL ELECTRIC: Was series resistance a limiting factor in your cells?

MR. EPSTEIN: No, but there was a great deal of it, as I implied from the capacity voltage curves.

QUESTION (NO NAME): Do you have any information about the crystalline imperfections present in your epitaxial layers?

MR. EPSTEIN: There are many imperfections. Also, the surfaces are not very smooth on the material that we have been making. In addition, there is a great deal of strain in the material resulting from the unequal thermal expansion coefficients of GaAs and GaP.

WOLF-HELIOTEK: You explained the 0.7 micron response by a two-step excitation process. If this is the case, how can you explain the low open circuit voltage associated with this cell?

MR. EPSTEIN: I'd rather not comment on that.

PERLMAN-RCA: I was wondering about the GaP layers. After you have grown them on the gallium arsenide, what preparation do you make of the surface prior to diffusion?

MR. EPSTEIN: We have tried a very light etch with hydrogen peroxide and sulphuric acid and water. We haven't found the most suitable etch yet.

PERLMAN-RCA: Is the resulting surface finish matte or polished?

MR. EPSTEIN: It's not polished and it's not matte. It's somewhere in between.

GOLDSTEIN-RCA: To continue the line of trying to find an explanation for the difference between 0.7 and 0.45 micron cells, I am wondering if you ran impurity analyses on your grown gallium phosphide material?

MR. EPSTEIN: No, we didn't have enough material. This is one of the things we are trying to do now.